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Document ID: US 6171497 B1

L2: Entry 1 of 5

File: USPT

Jan 9, 2001

US-PAT-NO: 6171497

DOCUMENT-IDENTIFIER: US 6171497 B1

TITLE: Thinly permeable composite reverse osmosis membrane

DATE - ISSUED: January 9, 2001

## INVENTOR - INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Hirose; Masahiko	Shiga			JP
Ohara; Tomomi	Shiga			JP
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US-CL-CURRENT: 210/500.38; 210/321.6, 210/321.74, 210/321.75, 210/490

[illegible]

2 Document ID: US 5698183 A

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File: USPT

Dec 16, 1997

US - PAT - NO: 5698183

DOCUMENT-IDENTIFIER: US 5698183 A

TITLE: Compositions comprising high loading water-dispersible UVA and/or UVB light-absorbing copolymer

DATE-ISSUED: December 16, 1997

## INVENTOR - INFORMATION:

INVENTOR- INFORMATION:				
NAME	CITY	STATE	ZIP CODE	COUNTRY
Langer; Matthew Evan	New City	NY		
Hessel; John Frederick	Metuchen	NJ		
Khorshahi; Ferial	Leonia	NJ		
Sinfield; Dennis Brian	North Bergen	NJ		

US-CL-CURRENT: 424-40; 424-6, 525-125

[illegible]

## 3 Document ID US 5250652 A

L2: Entry 3 of 5

File: USPT

Dec 5, 1987

US-PAT-NO: 5250652

DOCUMENT-IDENTIFIER: US 5250652 A

TITLE: Process for the preparation of UVA and/or UVB light-absorbing copolymer

DATE-ISSUED: September 5, 1987

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Langer; Matthew E.	New City	NY		
Knorshahi; Ferial	Leonia	NJ		

US-CL-CURRENT: 528/125; 528/128, 528/176, 528/183, 528/185, 528/189, 528/192, 528/193,  
528/194, 528/225, 528/272, 528/288, 528/292, 528/302, 528/303, 528/304, 528/305,  
528/308, 528/308.6, 528/332

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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## 4 Document ID US 4885091 A

L2: Entry 4 of 5

File: USPT

Dec 5, 1989

US-PAT-NO: 4885091

DOCUMENT-IDENTIFIER: US 4885091 A

TITLE: Process for the preparation of chlorine-resistant semipermeable membranes

DATE-ISSUED: December 5, 1989

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Swedo; Raymond J.	Mt. Prospect	IL		
Zupancic; Joseph J.	Bensenville	IL		

US-CL-CURRENT: 210-531.27; 264 41

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

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## 5 Document ID US 4695383 A

L2: Entry 5 of 5

File: USPT

Sep 22, 1987

US-PAT-NO: 4695383

DOCUMENT-IDENTIFIER: US 4695383 A

TITLE: Permsselective membrane

DATE-ISSUED: September 22, 1987

## INVENTOR-INFORMATION:

US-CL-CURRENT: 210/500.37; 210/500.23, 210/500.41, 521 114, 521 115, 521 114, 521 117

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L7: Entry 1 of 36

File USPT

Jan 8, 2002

DOCUMENT-IDENTIFIER: US 633701: B1

TITLE: Composite membrane and method for making the same

Abstract Text (1)

A composite membrane and method for making the same, comprising a porous support and a crosslinked polyamide surface. The subject membrane provides improved flux and/or selectivity. The subject membrane is further capable of operating at lower operating pressures. The subject method includes reacting a polyfunctional amine with a polyfunctional acyl halide to form a polyamide. The method includes the step of contacting a phosphorous containing compound with the polyfunctional acyl halide prior to and/or during the reaction between the polyfunctional acyl halide and a polyfunctional amine. The subject process is easily adapted to commercial scale manufacturing processes and is particularly suited for making nanofiltration and reverse osmosis composite membranes.

Brief Summary Text (6)

Among particularly useful membranes for reverse osmosis and nanofiltration applications are those in which the discriminating layer is a polyamide. The polyamide discriminating layer for reverse osmosis membranes is often obtained by an interfacial polycondensation reaction between a polyfunctional amine and a polyfunctional acyl halide as described in, for example, U.S. Pat. No. 4,277,344, which is incorporated herein by reference. In contrast to reverse osmosis membranes, the polyamide discriminating layer for nanofiltration membranes is typically obtained via an interfacial polymerization between a piperazine or an amine substituted piperidine or cyclohexane and a polyfunctional acyl halide as described in U.S. Pat. Nos. 4,769,148 and 4,889,394. Another way of obtaining polyamide discriminating layers suitable for nanofiltration is via the methods described in, for example, U.S. Pat. Nos. 4,765,897; 4,812,777; and 4,848,374. These patents describe changing a reverse osmosis membrane, such as that of U.S. Pat. No. 4,277,344, into a nanofiltration membrane.

Brief Summary Text (7)

Composite polyamide membranes are typically prepared by coating a porous support with a polyfunctional amine, most commonly coated from an aqueous solution. Although aqueous solutions are preferred, non-aqueous solutions may be utilized, such as acetyl nitrile and dimethylformamide (DMF). A polyfunctional acyl halide is subsequently coated on the support, typically from an organic solution. Although no specific order of addition is necessarily required, the aqueous amine solution is typically first coated on the porous support followed by the organic acyl halide solution. Although one or both of the polyfunctional amine and acyl halide may be applied to the porous support from a solution, they may alternatively be applied by other means such as by vapor deposition.

Brief Summary Text (8)

Means for improving the performance of membranes by the addition of constituents to the aqueous amine and/or organic acyl halide solutions are described in the literature. For example, U.S. Pat. No. 4,958,484, issued to Han, describes a method for increasing flux of a composite membrane by adding a polar aprotic solvent and an optional acid acceptor to the aqueous amine solution prior to interfacially polymerizing the amine with an polycarboxylic acid halide. Similarly, U.S. Pat. No. 5,889,426 to Hirose et al. describes the addition of selected alcohols, ethers, ketones, esters, halogenated hydrocarbons, and sulfur-containing compounds and sulfur-containing compounds having a molecular weight of 10 to 14 daltons, sup. 1-2 to either the aqueous amine solution or organic acyl halide solution prior to interfacial polymerization.

Brief Summary Text (9)

Methods of improving membrane performance by post-treatment are also known. For example, U.S. Pat. No. 5,576,612 to Jones et al. describes treating a polyamide composite membrane with an aqueous chlorinating agent to improve flux, lower salt passage, and/or increase membrane stability to water. U.S. Pat. No. 5,000,444 to Wilson discloses a process wherein the polyamide discriminating layer is treated with ammonia or selected amines, e.g., butylamine, cyclohexylamine, and 1,6-hexane diamine. U.S. Pat. No. 4,738,471 discloses the post-treatment of a membrane with a strong mineral acid to weakly treatment with a selection enhancing agent. U.S. Pat. Nos. 4,738,471, 5,000,444, and 5,576,612 are incorporated herein by reference.

#### Brief Summary Text (23):

The present invention provides an improved composite membrane and method for making the same including the non-sequential steps of coating a porous support with: (i) a solution containing a polyfunctional amine and (ii) a solution containing a polyfunctional acyl halide, wherein the polyfunctional amine and polyfunctional acyl halide are contacted with each other and react to form a polyamide layer on the porous support. The method includes the step of contacting a phosphorous containing compound with the polyfunctional acyl halide prior to and/or during the reaction between the polyfunctional acyl halide and polyfunctional amine.

#### Brief Summary Text (23):

One means for determining whether the subject phosphorous containing compound(s) have been successfully contacted with the acyl halide in accordance to the subject method is the presence of a "detectable quantity" of "retained" phosphorous in the polyamide membrane. The term "retained" phosphorous is intended to mean that phosphorous which remains associated (e.g., covalently bonded, complexed, weakly bound, etc.) with the polyamide membrane after being subjected to cleaning with pure water, e.g., passing pure water across the polyamide membrane at 25 degree C. for 24 hours at a pressure of about 70 pounds per square inch. Such cleaning removes transient sources of phosphorous which may be initially present but which do not contribute to the subject invention. For example, it is well known that phosphoric acid may be added to the amine solution and, prior to the reaction, some portion of the phosphoric acid may be present on the initial resulting membrane; however, as the phosphoric acid is not contacted with the acyl halide in manner which permits complexation, the phosphoric acid is not retained and is washed away from the membrane upon use or cleaning. Although such prior art uses of phosphoric acid may be used in conjunction with the subject invention, such prior art embodiments do not result in "retained" phosphorous as described above, nor the degree of improved membrane performance attributed to the subject invention.

#### Brief Summary Text (24):

The term "detectable quantity" is intended to mean a sufficient quantity of retained phosphorous is present such that it may be measured, identified or otherwise detected by quantitative or qualitative analysis. Detection of phosphorous in membranes can be made by way of any suitable analytical technique, however due to the relatively low quantities of phosphorous containing compounds utilized, relatively sensitive analytical techniques are preferred, e.g., X-ray fluorescence (XRF), secondary ion mass spectrometry, IR, and colorimetric analysis of the fully converted polyamide. One specific X-ray fluorescence detection methodology involves extracting a portion (e.g., 100 mg) of the polyamide polymer from the porous support, e.g., boiling the membrane in water for about 30 minutes followed by dissolving the porous support with an appropriate solvent, e.g., methylene chloride, and subsequently extensively extracting the polyamide in the same solvent. The polyamide may then be isolated and pressed into a disk (e.g., 13 mm dia and a die and an hydraulic press (10,000 lbs. load). The resulting disk is placed between two layers of polypropylene sample support film (e.g., 13 mm dia) and attached to a Chemplex 38 mm diameter XRF sample cup using a standard support ring. The sample can be measured in a plastic insert with a Pb mask. Measurements can be obtained on both sides of the disk and averaged together. Once prepared, the sample can be analyzed with a Philips PW1483 wavelength dispersive X-ray fluorescence spectrometer equipped with a scandium anode 3 KW X-ray tube. For measurement of Phosphorous, K alpha X-ray intensity the instrument can be operated under the following conditions: 50 kV, 50 mA, germanium crystal (2 $\theta$ =6.532 angstroms), gas flow proportional detector (argon/methane), upper and lower discriminator level 8-25% He purge. The Phosphorous K alpha peak can be measured at a 2 theta angle of 14.1-14.9 and backgrounds can be measured at + and - offsets of 1.5. Peak and background measurements are commonly taken for 10 seconds each.

#### Brief Summary Text (25):

In preferred embodiments, the subject polyamide composite membrane includes at least about 1 microgram (and more preferably at least 1 microgram, even more preferably 1

micrograms and in some embodiments at least 1 microgram of "retained" phosphorous per gram of polyamide. As indicated, the retained phosphorous is believed to be a result of the formation of a complex between the phosphorous containing compound and the acyl halide. Although dependent upon the relative reactivity of the polyamide layer, most embodiments of the subject invention will include at least 1 microgram of phosphorous per square meter of membrane, but more commonly more than about 1 microgram of phosphorous per square meter of membrane.

#### Brief Summary Text 25 :

The phosphorous containing compounds of the present invention are not particularly limited and different species of compounds may be used in combination. However, preferred species are non pyrophoric, sufficiently stable in air and water, the species do not decompose, degrade or significantly react with water or air within the time period of the subject method, and have suitable industrial hygiene properties, e.g., do not pose significant environmental hazards, do not require expensive handling requirements, do not pose significant safety concerns, etc. The subject phosphorous containing compounds are preferably "substantially soluble" in the organic solutions as described herein. The term "substantially soluble" is intended to mean that a sufficient quantity of the phosphorous containing compound dissolves in the solution to result in a membrane having improved flux, rejection and/or lower operating temperature compared to a control membrane prepared without the subject phosphorous containing compound. An additional indicia that the phosphorous containing compound is "substantially soluble" is the presence of a detectable quantity of retained phosphorous in the polyamide layer. When used at effective concentrations the subject phosphorous containing compounds preferably dissolve and form a single homogeneous phase within the organic solutions previously described. Preferred phosphorous containing compounds have a solubility parameter of from about 15 to about 26, and more preferably from 18 to 23 J.sup.1/2 cm.sup.-3/2.

#### Brief Summary Text 49 :

A variety of membrane shapes are commercially available and useful in the present invention. These include spiral wound, hollow fiber, tubular, or flat sheet type membranes. In regard to the composition of the membrane, often the discriminating layer has hygroscopic polymers other than the polyamide coated upon the surface of the discriminating layer. Among these polymers are anionic, cationic, neutral and zwitterionic such as polymeric surfactants, polyvinyl alcohol, polyethylene imine and polyacrylic acid.

#### Brief Summary Text 61 :

An embodiment described in U.S. Pat. No. 8,476,602, membrane stability to strong base can be achieved by maintaining flux and salt passage. can be achieved by contacting the membrane with a hypochlorite solution at a pH of at least 10.5. The optimal treatment time depends on the temperature and concentration of the hypochlorite used. At room temperature, conditions which achieve the stated goals can generally be found within the ranges of 10 minutes to 5 hours and at concentrations of 28. to 10,000 ppm by weight of hypochlorite, measured as chlorine. Preferred concentrations of hypochlorite are 500 to 7,000 ppm; preferred exposure times are 30 minutes to three hours. In a preferred embodiment the membrane is subjected to a heat treatment before being exposed to the aforementioned chlorine treatment. The membranes are heated in water at a temperature of 40.degree. C. to 100.degree. C. for times of 30 seconds to 24 hours. The heat treatment results in a further lowering of the salt passage and the removal of impurities contained in the membrane which otherwise may interfere in the beneficial results of the chlorine treatment. Depending on the application desired, the two treatment conditions can be adjusted within the ranges stated such that the salt passage is improved while maintaining or even improving flux over either treatment alone. The order in which the two treatments are conducted is critical since heat treating the membrane simultaneously with or subsequently to the chlorine treatment does not provide the improved results obtained by first heat treating the membrane followed by the chlorine treatment.

#### Brief Summary Text 67 :

In a preferred embodiment the polyamide discriminating layer may be in solution, neat, or even a gas phase as long as it can be contacted with the polyamide. Gas phases may typically be comprised of lower molecular weight amines such as ammonia, methylamine, and dimethylamine. The solvent may be any solvent in which the amine is soluble so long as the flux enhancement and the performance of the membrane is not hindered by contact with the solvent. Typical solvents may include water and organic compounds such as alcohols and hydrocarbons provided the support is not dissolved by the solvent.

generally, because of its ease of handling and its availability, water is employed if a solvent is desired.

#### Brief Summary Text 1991:

In general, the longer the time of contact and the higher the concentration of the amine, the greater the increase in flux. After a prolonged time of contact, the flux will reach a maximum increase and will no longer increase. At this point, the membrane may be removed and stored in the amine. The time to reach the maximum increase in flux depends upon the particular amine employed, the concentration of the amine, and the temperature of contact and is ascertainable by one skilled in the art without undue experimentation by utilizing the general trends disclosed above. For most amines and concentrations, the flux of the membrane will be maximized once the discriminating layer has been contacted for about 8 days with the amine. If it is desired to shorten the minimum length of time of contact, then the surface temperature of the polyamide discriminating layer may be increased. Although this applies generally, it is particularly advantageous if low concentrations of an amine which might require a long contacting time are being employed. Although temperature from about 1 degree. C. to about 70 degree. C. are most conveniently used, increased temperatures may shorten the necessary contacting time. The increased temperatures should not be so high that the membrane's performance is reduced, i.e., not above about 130 degree. C. Typical temperatures which will hasten the flux effect of the membrane are from at least about 30 degree. C., preferably at least about 60 degree. C. to about 120 degree. C. These temperatures may be reached by contacting the amine with the polyamide discriminating layer in a device such as an oven or a dryer. Typical ovens or dryers which may be employed include convection, infrared, or forced air dryers.

#### Brief Summary Text 1992:

As used herein the following terms have the definitions provided: "rejection rate" is the percentage of a particular dissolved or dispersed material (i.e., solute) which does not pass through the membrane with the solvent. The rejection rate is equal to 100 minus the percentage of dissolved or dispersed material which passes through the membrane, i.e., solute passage, "salt passage" if the dissolved material is a salt. "Flux" is the flow rate per unit area at which solvent, typically water, passes through the membrane. "Reverse osmosis membrane" is a membrane which has a rejection rate for NaCl of from about 95 to about 100 percent. "Nanofiltration membrane" is a membrane which has a rejection rate for NaCl of from about 5 to about 95 percent and has a rejection rate for at least one divalent ion or organic compound of from about 20 to about 100 percent. "Polyamide" is a polymer in which amide linkages (-C(=O)NH-) occur along the molecular chain.

#### CLAIMS:

1. A method for making a composite membrane comprising the non-sequential steps of coating a porous support with: (i) a solution containing a polyfunctional amine and (ii) a solution containing a polyfunctional acyl halide, wherein the polyfunctional amine and polyfunctional acyl halide are contacted with each other and react to form a polyamide layer on the porous support, the process being characterized by the step of contacting a phosphorous containing compound with the polyfunctional acyl halide prior to the reaction between the polyfunctional acyl halide and polyfunctional amine wherein the phosphorous containing compound has a solubility parameter of from about 15 to about 20, and a pH of at least 2.
2. The method of claim 1 wherein the polyamide layer is contacted with a solution containing from 10 to 10,000 ppm of hypochlorite ion at a pH of at least 10.5.
3. The method of claim 2 wherein the polyamide layer is heat treated by contact with water at a temperature of 40 degree. C. to 100 degree. C. before contacting the membrane solution with the containing hypochlorite ion.

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L18 and polyamide

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<u>L17</u>	hypochlorite and hypobromite	972	<u>L17</u>
<u>L16</u>	L15 and 17	0	<u>L16</u>
<u>L15</u>	11 and bromine	37	<u>L15</u>
<u>L14</u>	L7 and bromine	0	<u>L14</u>
<u>L13</u>	L12 and 11	0	<u>L13</u>
<u>L12</u>	L11 and membrane	3	<u>L12</u>
<u>L11</u>	hypobromic acid	25	<u>L11</u>
<u>L10</u>	L9 and 11	0	<u>L10</u>
<u>L9</u>	hypobromous	467	<u>L9</u>
<u>L8</u>	L7 and posttreatment	0	<u>L8</u>
<u>L7</u>	11 and hypochlorite	38	<u>L7</u>
<u>L6</u>	11 and hypobromide	0	<u>L6</u>
<u>L5</u>	L1 and bromination	1	<u>L5</u>
<u>L4</u>	L1 and bromine	37	<u>L4</u>
<u>L3</u>	L1 and hypobromine	0	<u>L3</u>
<u>L2</u>	L1 and hypochloride	5	<u>L2</u>
<u>L1</u>	membrane same polyamide and interfacial	387	<u>L1</u>

END OF SEARCH HISTORY